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COMMUNICATION

Capture and activation of aerial CO_2 by carbamoylation of L-threonine in a Ag(I) supramolecular framework†

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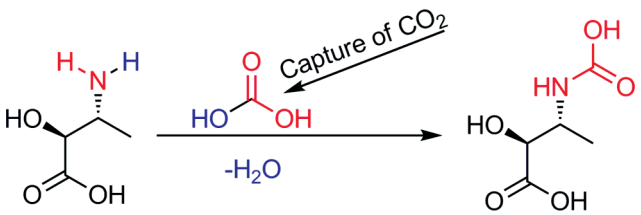
An ultrasonic reaction of Ag_2O, 4,4′-bipyridine (bipy) and (2*S*, 3*R*)-3-amino-2-hydroxybutanoic acid (L-Thr) gives an unexpected Ag(I) supramolecular framework, $\{[Ag_3(bipy)_3(cahba)]\cdot HCO_3\cdot 10H_2O\}_n$ (1), in which the (2*S*, 3*R*)-3-(carboxyamino)-2-hydroxybutanoic acid (H_2cahba) is a carbamate derivative of L-Thr, obtained *via in situ* transformation of amino group of L-Thr into carbamate by means of CO_2 uptake.

The fixation, activation and utilization of CO_2 has evoked intense interest as (i) excess CO_2 causes serious environmental issues, (ii) CO_2 can be a promising successor of limited carbon resources (coal, petroleum and natural gas), (iii) CO_2 can be used to mimic photosynthesis and enzyme-catalyzed reactions in the lab which would be helpful in comprehending photosynthetic processes in nature and in utilizing enzyme-analogous reactions for chemical syntheses.[1] In biological CO_2 fixation (the Calvin cycle),[2] the carbamate species is a key component formed by reaction of the lysine side chain with CO_2, which is catalyzed by Mg(II)-containing enzymes, such as ribolose-1,5-bisphosphate carboxylase/oxygenase (rubisco).[3] Although fixation of CO_2 as HCO_3^- or CO_3^{2-} containing complexes is common in the literature,[4] the transformation of CO_2 into carbamate species in an artificial system is still hard to access due to its instability.[5] When compared to the abundant Zn(II), Cd(II), Cu(II), Co(II), Ni(II) and La(III) complexes,[6] utilizing Ag(I) complexes to fix and activate CO_2 is still very sparse.[7] Herein, we present a Ag(I) supramolecular complex $\{[Ag_3(bipy)_3(cahba)]\cdot HCO_3\cdot 10H_2O\}_n$ (**1**) which unprecedentedly exhibits the fixation and activation of aerial CO_2 *via* the complexation process between L-Thr and CO_2 in an artificial system (Scheme 1).

Ultrasonic treatment of a mixture of Ag_2O, bipy and L-Thr in methanol–H_2O (v/v = 1 : 1) solvent with an initial pH of 12 in air gave complex **1** by slow evaporation. Subsequent crystallographic studies confirmed the coexistence of two unexpected alien species, HCO_3^- and carbamate derivative of L-Thr in the crystal structure of **1**. The compositions of **1** were further deduced from single-crystal X-ray diffraction,‡ elemental analyses and IR spectra. The solid FT–IR spectra (Fig. S1, ESI)† of complex **1** shows the a very intense broad band around 3450 cm^{-1} attributed to the presence of water molecules. The asymmetric and symmetric stretching vibrations of the carboxyl group are 1594 and 1403 cm^{-1}, respectively. There is no band in the 1690–1730 cm^{-1} region, indicating complete deprotonation of the carboxyl groups.[16] The phase purity of **1** is sustained by its powder X-ray diffraction pattern, which is consistent with that simulated on the basis of the single-crystal X-ray diffraction data (Fig. S2, ESI).†



Scheme 1 *In situ* generation of the carbamate derivative of L-Thr by means of aerial CO_2 uptake.

Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the acentric monoclinic $P2_1$ space group with an asymmetric unit that contains three crystallographically independent Ag(I) ions, three bipy ligands, one cahba, one HCO_3^- and ten H_2O molecules (Fig. 1). The charge neutrality is achieved by two deprotonated carboxyl groups of H_2cahba and one HCO_3^-. It is worth noting that the C36–O6 distance (1.361(5) Å) is much longer

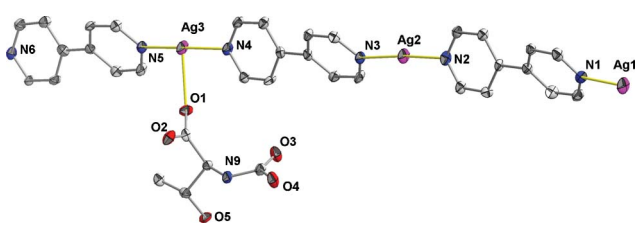


Fig. 1 ORTEP drawing of the asymmetric unit of complex **1** with thermal ellipsoids at 50% probability level. The hydrogen atoms and lattice water molecules are omitted for clarity.

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† Electronic supplementary information (ESI) available: Crystallographic data in CIF format, additional figures of the structure, experiments for the synthesis of complex **1** and X-ray diffraction, PXRD, IR, TG and UV-vis for complex **1**. CCDC reference numbers 796862. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10571j

than the other two $C_{bicarbonate}$–O distances (1.258(6) and 1.263(6) Å) which assist us to distinguish H_2CO_3, HCO_3^- and CO_3^{2-}. The Ag1, Ag2 and Ag3 are located in linear (two N_{bipy}), T-shaped (two N_{bipy} and one O_{cahba}) and distorted seesaw (two N_{bipy}, one O_{cahba} and one O_{water}) coordination geometries, respectively. The Ag–N and Ag–O bond lengths fall in the ranges of 2.138(6)–2.192(4) and 2.579(4)–2.659(4) Å, respectively. All the bond lengths are well-matched to those observed in similar complexes.[8] The largest angles around Ag1 and Ag2 are 167.1(2) and 174.99(19)°, respectively. Recently, Houser and co-workers have proposed an angular index (τ_4) for a four-coordinate metal center, which is defined by the equation $\tau_4 = [360 - (\alpha + \beta)]/141$ (α and β are the two largest angles around the metal).[9] According to the value of τ_4, the geometry of the four-coordinate center can be described as tetrahedral ($\tau_4 = 1$), trigonal pyramidal ($\tau_4 = 0.85$), seesaw ($\tau_4 = 0.64, 0.50, 0.18, 0.07$), and square planar ($\tau_4 = 0$). The τ_4 value for Ag3 is calculated to be 0.44 (α and β are 171.54(18) and 125.73(13)°, respectively). So the geometry around Ag3 can be best described as a distorted seesaw. The pyridyl rings in every bipy ligand are not co-planar and give an average dihedral angle of 30.6(8)°. The bipy ligands link the Ag(I) ions to form a 1D chain on which the cahba ligands dangle. Although one cahba ligand has five potential coordination sites (four $O_{carboxyl}$ and one N_{imino}), only two monodentate O atoms on one carboxyl group coordinate with Ag(I), consequently, no increase of dimensionality is observed in complex **1**.

Based on the view of supramolecular interactions, the adjacent 1D chains are packed into a 2D sheet through weak Ag···Ag (Ag2···Ag3^{viii} = 3.4193(9) Å) and π···π aromatic stacking (average centroid···centroid distance: 3.613(3) Å, Table S3 and Fig. S3, ESI)† interactions. Furthermore, between the adjacent 2D Ag-bipy sheet, the uncoordinated groups of the cahba ligand combine with the lattice water molecules and HCO_3^- anions to form a 2D H_2O/HCO_3^-/cahba anionic sheet (Fig. 2a). It is worth noting that a well-resolved infinite water aggregate exist in the 2D anionic sheet. As shown in Fig. 2b, this 1D water aggregate is comprised of three kinds of subunits, V-shaped trimer (O1 W, O3 W O5 W), chain-like trimer (O8 W, O9 W, O10 W) and cyclic tetramer (O2 W, O4 W, O6 W O7 W). The tetramer and V-shaped trimer link together through a O5W–H5WB···O4 W (2.800(5) Å) hydrogen bond, and the chain-like trimer links V-shaped trimer and tetramer through O10W–H10C···O5W^{iv} (2.917(6) Å) and O4W–H4WB···O8 W (2.714(5) Å) hydrogen bonds to form the infinite water aggregate. The hydrogen-bonded O···O separations in the 1D water aggregate span the range 2.714(5)–2.947(6) Å with an average value of 2.812(5) Å, which is in the range of the corresponding values in I_h ice at 183 K (2.759(2) Å)[10] and liquid water (2.851(3) Å).[11] As we know, the elusive carbamic acids are labile compounds that easily convert back to the parent amine and CO_2.[6d] Their synthesis has been accomplished only very recently.[12] So the survival of carbamate moiety is undoubtedly associated with the abundant hydrogen bonds. (Symmetry code: (iv) $x + 1$, y, z.)

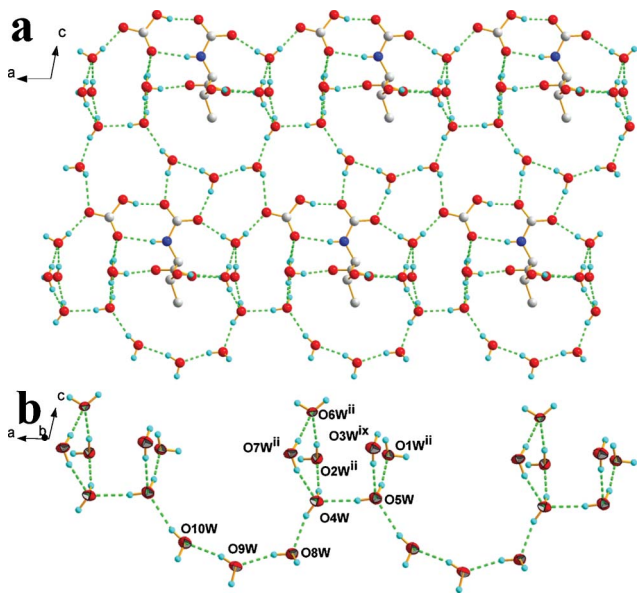

Fig. 2 (a) Ball-and-stick diagram showing the 2D anionic H_2O/HCO_3^-/cahba sheet in which hydrogen bonds are indicated by green dashed lines. (b) ORTEP drawing of the 1D infinite water aggregate with thermal ellipsoids at 50% probability level. (Symmetry codes: (ii) x, y, $z + 1$; (ix) $1 - x$, $0.5 + y$, $-1 - z$.)

The most fascinating feature of complex **1** contains two aspects: (i) fixation of CO_2 as HCO_3^- and (ii) activate CO_2 as carbamate species. Firstly, fixation of CO_2 as HCO_3^- is unambiguously related to the alkaline solution involving the hydration of aerial CO_2 to give H_2CO_3, which in turn undergoes deprotonation in alkaline conditions (25% NH_3 aqueous solution used). This process can also be realized naturally by the enzyme carbonic anhydrase containing an active Zn(II) center.[13] Secondly, although the carbamate moiety does not coordinate with the Ag(I) center, we still believe that Ag(I) is a crucial factor for the formation of the carbamate species. To prove this, the reaction in the absence of Ag_2O under similar conditions was performed. The resulting colourless single crystals were identified to be a reported proton transferred L-Thr by single-crystal X-ray diffraction.[14] Based on this result, we conclude that the formation of the carbamate species can not be achieved without Ag(I). So we would thus like to propose a possible mechanism, that is, Ag(I)-assisted formation of carbamate species in an alkaline environment. As far as we know, the pK_a value of the primary amine is very high, however metal binding to the free electron pair at the amino group causes a dramatic increase in acidity of these protons.[15] As a consequence, the formation of the potential imine anion is facile and quickly to electrophilic attack of CO_2 or HCO_3^-. The formation of the imine anion under similar conditions was also observed in our previous work in which the primary aromatic amine was deprotonated to coordinate with Ag(I).[16] Notably, it is also unavoidable that CO_2 or HCO_3^- can somewhat be polarized by the Lewis acid Ag(I) ion through a coordination effect, which also facilitates the occurrence of the electrophilic reaction. Our result presented here is the first example of formation of carbamate species from primary amine with the aid of Ag(I) by the aerial CO_2 uptake.

The thermogravimetric (TG) analysis was performed in a N_2 atmosphere on polycrystalline samples of complex **1** and the TG curves are shown in Fig. S4 (ESI).† The TG curve of **1** shows the first weight loss of 21.74% in the temperature range of 25–105 °C, which indicates the loss of ten lattice water molecules and one HCO_3^- per formula unit (calcd: 20.19%), and then the metal–organic framework starts to decompose accompanying loss of organic ligands. The residual weight of 28.71% is consistent with that of 27.09% calculated for metallic silver.

Both the diffuse reflectance and photoluminescence spectra of **1** were measured in solid state at room temperature. As shown in Fig. S5,† the absorption bands at 270 and 360 nm correspond to $\pi \rightarrow \pi^*$ transition of the bipy ligand. The pale yellow color of powder of **1** is consistent with the weak absorption in *ca.* 450 nm which is associated with the ligand–to–metal charge transfer (LMCT) absorption band. Excitation of solid powder sample **1** at 330 nm produces an emission with a maximum at *ca.* 420 nm (Fig. S6, ESI).† When compared to the photoluminescence spectrum of the free bipy ligand (λ_{em} = 436 nm), the emission bands of **1** is blue-shifted by more than 16 nm, which could be assigned to $\pi^* \rightarrow \pi$ electronic transition of bipy ligand.[17] The blue shift of the emission compared with that of free bipy ligand may be attributed to the ligation of the bipy ligands to Ag(I) centers by enhancing its conformational rigidity and decreasing the non-radiative energy loss.[17d]

In conclusion, we realized the fixation and activation of CO_2 as carbamate species in the artificial Ag/L-Thr/bipy system. The results helped us not only to understand the fundamental processes of natural fixation of CO_2 and to mimic them in artificial systems but also to search for crucial steps for CO_2-based chemical syntheses.

Acknowledgements

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‡ Crystal data for **1** $\{[Ag_3(bipy)_3(cahba)]\cdot HCO_3\cdot 10H_2O\}_n$: M_r = 1194.46, colourless, monoclinic, space group $P2_1$ (no. 4), a = 10.798(2) Å, b = 17.973(4) Å, c = 11.474(2) Å, β = 100.40(3)°, V = 2190.2(8) Å^3, Z = 2, D_{calcd} = 1.811 g cm^{-3}, μ(Mo-Kα) = 1.411 mm^{-1}. A total of 16 427 reflections were collected on a Rigaku R-AXIS RAPID Image Plate diffractometer using the ω scan mode with Mo-Kα radiation λ = 0.71073 Å at 173(2) K, of which 7645 were independent reflections (R_{int} = 0.0496). Structure solution and refinement were routine. Final R indices for the 6267 observed reflections ($I > 2\sigma(I)$): R_1 = 0.0346, wR_2 = 0.0813; max./min. residual electron density, 1.155/–0.874 e Å^{-3}.

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